Missouri Department of Natural Resources
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Monitored Natural Attenuation of Groundwater Contamination at Brownfields-Voluntary Cleanup Program Sites

Hazardous Waste Program technical bulletin 7/2003

The chemical, physical and biological processes involved in natural attenuation of environmental contamination are rapidly becoming better understood. With this greater understanding, interest is growing in the use of monitored natural attenuation (MNA) as a remedy of choice in treating groundwater at sites contaminated with hazardous substances.

This technical bulletin provides guidance on the use of MNA to participants in the department's Brownfields-Voluntary Cleanup Program (VCP) conducting remediation pursuant to 10 CSR 25-15.010.

While many aspects of this guidance may also apply to sites being addressed under the oversight of other departmental regulatory programs, it is currently intended for use only by VCP participants. Those working with other regulatory programs should check with representatives of those programs prior to using this guidance.

What is Monitored Natural Attenuation?

The term monitored natural attenuation as used in this technical bulletin refers to the reliance on natural processes to achieve groundwater cleanup goals within a reasonable time frame. These include chemical, physical, and biological processes that act to reduce the mass, volume, mobility, toxicity, or concentration of groundwater contaminants.

Other terms sometimes associated with natural attenuation include passive remediation or bioremediation, intrinsic remediation or bioremediation, reductive dehalogenation, and natural assimilation. However, many of these terms refer only to specific aspects of the natural attenuation process. For the purposes of this technical bulletin, the term MNA will be used to encompass all aspects of the natural attenuation process.

Most aquifers have a built-in capacity for biodegradation, dispersion, volatilization, sorption and other processes that affect groundwater contaminants. Used as remediation, MNA is a demonstration that this built-in capacity will reduce contaminant levels within a reasonable time frame and before the contaminants present an unacceptable risk to human health or the environment, or exceed approved cleanup levels at established points of compliance.

The effectiveness of MNA has been clearly and routinely documented at petroleum contaminated sites. But it may also be an important factor at sites contaminated with chlorinated solvents, inorganics including metals and radionuclides, and mixtures of these contaminants.

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Not a Do Nothing Approach

The monitored aspect of MNA refers to the fact that extensive sampling and modeling efforts are typically needed to demonstrate that natural attenuation will be sufficient to meet site cleanup goals. In this regard, it is important to recognize that MNA is not a no action alternative. Further, some form of source control measures is almost always necessary at sites with groundwater contamination. MNA is often used as a complementary technique along with more active remedial measures. The most typical example is that of a site where active remediation is applied in high concentration areas of a plume, while MNA is used in low concentration areas or as a follow-up to active remedial measures.

Pros and Cons of MNA

When evaluating remedial measures, the potential advantages and disadvantages of MNA relative to other options should be carefully considered before selecting the most appropriate measures. Generally, MNA should be selected only where it will meet the approved cleanup objectives within a time frame that is reasonable compared to that offered by other methods. Sites where the contaminant plume is no longer expanding, or is shrinking, will be the most appropriate candidates for the use of MNA remedies.

Advantages of MNA:

- Reduced overall remediation costs;
- Less intrusive, as fewer surface structures are required;
- Generation of less remediation waste;
- Results in the destruction of contaminants;
- Reduced potential for cross-media transfer of contaminants;
- Reduced risk of human exposure relative to more active remediation; and
- Reduced disturbance to ecological receptors.

Disadvantages of MNA:

- Site characterization may be more complex and costly;
- Longer time frame is generally required to achieve cleanup goals;
- Generation of toxic or mobile transformation products;
- Hydrologic and geochemical conditions may change over time, thereby reducing effectiveness;
- Higher level of public education and outreach required to gain public acceptance;
- Long-term performance monitoring is generally more extensive; and
- Institutional controls are usually necessary.

Implementation of MNA

The following guidance is based on the department’s experience with the use of MNA at VCP sites, and on the sources cited in the References below.

Source Removal

Treatment and control of contaminant sources should be evaluated at all VCP sites. This is especially true at sites where MNA is being considered. Contaminant sources that are not addressed may continue to leach at significant levels into groundwater. Since MNA typically involves a longer time frame than other more active remedial approaches, such persistent source areas may unacceptably extend the time needed for MNA to achieve approved cleanup goals. The VCP expects that source control or treatment measures will be evaluated at all sites, and that measures will be taken at most sites employing MNA as part of the remedy. Measures for addressing contaminant sources are numerous, but some of those most commonly used at VCP sites include:

Excavation
Non-aqueous phase recovery
Hydraulic containment
Enhanced biodegradation
Permeable reactive barrier
Bioventing
Air sparging
Soil vapor extraction
In situ chemical destruction

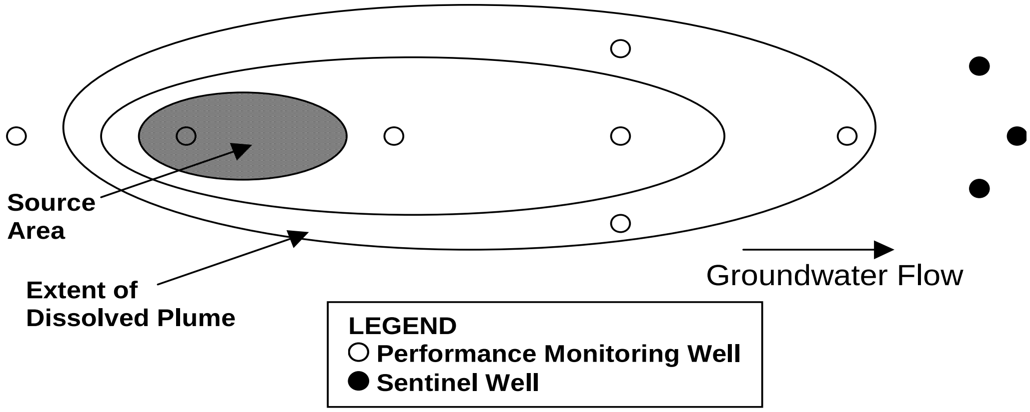
Demonstrating Effectiveness

Demonstrating the efficacy of MNA will typically be an iterative process that includes full and detailed characterization of the site, development of a conceptual model, and an analysis to determine whether MNA will be sufficient to achieve cleanup goals. Demonstrating the effectiveness of natural attenuation usually require a higher level of site characterization than that needed to support more active remedial measures. Similarly, sites with contaminants that do not tend to readily biodegrade will usually require a relatively higher level of site characterization than those with more biodegradable contaminants. The extent of investigation necessary to adequately characterize a site is highly site specific and will depend on the nature of contamination, hydrogeologic complexity, proximity of receptors, and other factors.

Site Characterization

In general, site characterization should include the collection of data in three spatial dimensions over time such that an adequate understanding can be gained of the nature and distribution of both the contaminant source areas and the groundwater plume. Site characterization should provide information on hydrogeologic parameters such as hydraulic conductivity, hydraulic gradients, and potential migration pathways to human and ecological receptors; geologic information on the nature and distribution of subsurface materials; groundwater geochemical data; and information on the location, extent, and concentration of dissolved contaminants. The number and location of sampling points required to achieve this understanding will be established site specifically with VCP input and approval. The minimum for most sites will include an upgradient well, at least one transect of wells screened within the longitudinal axis of the plume, and one transect screened within the transverse axis of the plume as shown below. Groundwater investigation must include sampling and analysis for the contaminants of interest, their daughter products, and other indicators important for demonstrating natural attenuation.

Generalized Monitoring Well Network



These may include hydrogen, methane, ethane, ethene, oxygen, redox potential, pH, conductivity, organic carbon, iron, manganese, chloride, nitrate, sulfate, hydrogen sulfide, alkalinity, and others. The specific analytes and frequency of monitoring required will be determined site specifically, and may be reduced following an initial period of monitoring with the approval of the VCP.

Conceptual Model

The site characterization data should be integrated into a conceptual model of the site. This is a three dimensional representation that integrates information on hydrogeologic conditions and the sources, fate, and transport of contaminants. The conceptual model will provide a framework for assessing remedial options (including MNA), and will address how MNA processes will perform to meet cleanup goals. The formation of a conceptual model should begin early in the site characterization process, and be continually refined as new data are available.

Using the conceptual model along with site characterization data, the potential efficacy of MNA as a remedy can be evaluated. The two primary lines of evidence used to evaluate MNA are 1) decreasing trend in contaminant mass and concentration over time, and 2) existence of geochemical and hydrogeologic conditions favorable for natural attenuation processes.

MNA Screening

The VCP recommends evaluating initial site characterization data using a screening approach to make a preliminary determination of whether further assessment of MNA as a remedy is warranted. The screening analysis should:

1. Determine whether geochemical and hydrogeologic conditions are favorable for natural attenuation of the contaminants;
2. Estimate the rate of contaminant attenuation;
3. Estimate the rate of contaminant migration compared to the estimated rate of attenuation; and
4. Determine whether the predicted rate of attenuation will meet the clean up goal in a reasonable time frame and without unacceptable risk to human health and the environment.

The U.S. Environmental Protection Agency has published a site-scoring tool for use when screening chlorinated solvent-contaminated sites for MNA (References 2,4). Methods for screening petroleum-contaminated sites are found in References 1,3,5,6. Simple analytic computer models may be useful in developing preliminary estimates of contaminant migration and attenuation over time. Examples of these models include BIOCHLOR and BIOSCREEN, which are available at http://www.epa.gov/ada/models.htm. These models are fairly limited in application due to the simplifications required to limit their input data requirements and thereby make them comparatively easy to use in some cases. It may be necessary to also employ more complex numerical models in order to better account for site complexity and improve estimates of attenuation rates.

If results of the site screening are favorable, a more detailed site characterization and refinement of the conceptual model may be necessary to fill in data gaps and reduce uncertainty in the initial predictions of contaminant attenuation rates. The estimate of contaminant biodegradation/attenuation rate is a critical component of determining whether MNA will be an adequate remedy. There are several methods for developing estimates of contaminant biodegradation and attenuation rates (see References below). These methods require varying degrees of site characterization, and produce estimates of varying accuracy depending on the specific site conditions. The VCP strongly recommends that several techniques be used together and the results compared to develop a better overall estimate.

It is important to note that groundwater in certain areas of Missouri occurs in complex geologic systems that may preclude reliance on an MNA remedy. The typical example is groundwater moving through highly fractured or karstic rock aquifers. In these systems, the cost of monitoring required to adequately identify preferential contaminant flow pathways and estimate rates of natural attenuation could easily exceed the costs of implementing other more active remediation techniques.

Performance Monitoring

If MNA is implemented at a site, monitoring to evaluate its effectiveness and ensure the protection of human health and the environment is critical. Performance monitoring is even more important for MNA than other types of remedies due to the typically longer timeframes and greater uncertainties associated with MNA. A performance monitoring program will be an integral part of all approved MNA remedies.
The monitoring program should be designed to accomplish the following:

- Demonstrate that natural attenuation is progressing as predicted;
- Verify that the plume is not expanding;
- Identify any toxic and/or mobile transformation products;
- Verify no unacceptable impact to downgradient receptors;
- Detect significant changes in relevant environmental conditions;
- Detect any new releases of contaminants;
- Demonstrate the efficacy of any institutional controls used and;
- Verify the attainment of cleanup goals.

Monitoring wells in this program include, but are not necessarily limited to, those placed to measure changes in the nature of the plume, and sentinel wells strategically placed to detect migration of contaminants outside an acceptable predicted area.

The frequency of performance monitoring and the monitoring parameters is typically determined on a site-specific basis. Performance monitoring should continue until the cleanup goals are achieved.

Contingency Planning

An approved plan for the use of MNA will include contingency planning provisions. Contingency planning includes specification of measures to be taken that will function as a back-up in the event that MNA fails to perform as anticipated. These measures may specify an intensification of monitoring activities, active enhancement of MNA processes, use of engineered barriers, or employment of remedial techniques entirely different from MNA, among many others.

The VCP recommends that one or more trigger criteria be established that will serve to signal unacceptable performance of MNA and indicate when the contingency measures should be implemented. Examples of such triggers include but are not limited to:

- Plume contaminant concentrations exhibit an unpredicted increasing trend;
- Plume contaminant concentrations do not decrease at a sufficiently rapid rate to meet cleanup goals within an acceptable time frame;
- Plume contaminants are detected in sentinel wells; and
- Changes in land and/or groundwater use that affects the protectiveness of the MNA remedy.
- A contingency plan should be included in the Remedial Action Plan.

Presentation of Data

It is the responsibility of the VCP participant to not only provide the data necessary to demonstrate the efficacy of MNA, but to analyze, interpret and present that data in a manner that facilitates the VCP's approval process.

The CALM guidance document provides a list of the basic report components. The following is not intended as an inclusive list, but rather highlights some additional components necessary at most sites to support a demonstration of MNA.

- Three dimensional conceptual model of the site presented in both discussion and graphical formats;
- Tabular summaries of raw laboratory data;
- Potentiometric water surface maps for each sampling event;
- Site maps including presentation of sampling points and laboratory data.;
- Isopleth maps (by depth and/or time as applicable) of parent contaminants, daughter products, electron acceptors/donors, and other relevant geochemical parameters;
- Isopach maps showing thickness and distribution of NAPL if present; and
- Geologic cross sections; both parallel and perpendicular to the plume axis.

Obtaining Site Closure

The conditions for obtaining closure of a site within the VCP using MNA to address groundwater contamination vary depending on whether the plume is contained within or extends beyond the VCP site boundaries. The following discussion presuppose that all other relevant criteria regarding MNA as discussed above have been met.

Plume is contained within the VCP site boundaries.

- Unrestricted site closure will be approved when groundwater contaminant levels across the entire plume are reduced below the Tier 1 groundwater target concentrations (GTARC) found in the most recent revision of the *Cleanup Levels for Missouri* (CALM) guidance document. Closure of sites with contaminant concentrations exceeding the Tier 1 GTARC may be allowed on a site-specific basis with the execution of appropriate institutional controls. This may be accomplished using a Tier 3 approach. Additional information on institutional controls may be found in the department's CALM document.

Plume extends across the VCP site boundaries.

- The participant notifies in writing all affected property owners of the contamination. VCP must approve the content of the notification letter.
- The participant obtains written permission from all affected property owners providing access to both DNR and the participant for the purposes of conducting plume delineation and, in most cases, installing permanent monitoring points.
- Unrestricted site closure will be approved once plume concentrations have been reduced below the Tier 1 GTARC across the entire plume (off and on-site).
- Closure of sites prior to achieving the Tier 1 GTARC (either on-site, off-site, or both) may be approved on a site-specific basis with the execution of appropriate institutional controls for both the VCP site and all other affected properties.
- Closure of sites with on-site plume concentrations exceeding the Tier 1 GTARC, but where off-site concentrations have been reduced below the CALM Tier 1 GTARC, may be approved on a site-specific basis with the execution of appropriate institutional controls pertaining to the VCP site only.

References

1. *Interim Guidance on Natural Attenuation For Petroleum Releases,* Wisconsin Department of Natural Resources, Bureau for Remediation and Redevelopment, PUB-RR-614, October 1999.
http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/RR614.pdf

2. *Natural Attenuation of Chlorinated Solvents in Ground Water*, Minnesota Pollution Control Agency, Site Remediation Section, May 2000.
http://www.pca.state.mn.us/cleanup/pubs/natatten.pdf

3. *Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites*, American Society for Testing and Materials, ASTM E-1943-98, 1998.

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6. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*, EPA Office of Solid Waste and Emergency Response Directive 9200.4-17P, April 21, 1999.
http://www.epa.gov/swerust1/directiv/d9200417.htm

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